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ARIZONA UNIV TUCSON DEPT OF CHEMISTRY
ELECTRICAL AND ELECTROCHEMICAL BEHAVIOR OF FILLED POLYMERIC FIL--ETC(U)
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FINAL TECHNICAL REPORT

6 ELECTRICAL AND ELECTROCHEMICAL BEHAVIOR
OF FILLED POLYMERIC FILMS.

Principal Investigator: Henry Freiser, Professor of Chemistry
University of Arizona
Department of Chemistry
Tucson, Arizona 85721

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Electrical conductivity of plasticized polyvinylchloride films containing valinomycin and potassium salts have been measured at various temperatures and pressures in order to obtain the conduction activation energies and volumes. These electrical properties change significantly at the glass transition temperature (T_g) of the polymer. For the first time, a detailed correlation of the T_g and the electrochemical behavior of the K⁺-valinomycin electrode has been obtained. (CONTINUED ON SECOND SHEET)

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CONTINUATION OF BLOCK 20. ABSTRACT

The study of filled polymeric films as sensitive temperature change indicators revealed that while the films were indeed sensitive, their signal/noise ratio was not as good as commercial thermistors.

The present investigation of the nature and mechanism of the conductivity of polymeric films incorporating various organic solvent-compatibilizing salts and complexes was inspired initially by our research in the area of ion selective electrodes. Ion selective electrodes (ISE), one of the most exciting recent developments in electrochemistry, permit rapid, reliable, selective, and sensitive potentiometric sensing of a wide number of inorganic (1, 2) and organic (3) cations and anions as well as of ionogenic species (e.g., of CS_2 ; $\text{CS}_2 + \text{R}_3\text{NH}^+ + \text{R}_3\text{NC}_2\text{H}_5^-$) (3). In the course of our ISE work we discovered that a metallic conductor (Cu, Pt, Ag, etc.), when coated with a suitable polymer (polyvinylmethacrylate, epoxy) in which a suitable organic salt was dissolved, would serve as an ion selective electrode in a manner equivalent to or in many cases, (4, 5) superior to the conventional "barrel" type of "filled membrane" ion selective electrode. Our ion selective electrodes, termed "coated wire" electrodes, have the further structural advantages of simplicity and concomitant very low cost, of ruggedness so that they can be used in various field applications (including in situ oceanographic measurements as will be described later), and of miniaturization to a point where they could serve in intracellular measurements. Having no internal reference solution, the coated wire electrodes can be placed in any attitude (the barrel type must be mounted vertically or nearly so).

The mechanism of electrode behavior of the coated wire electrode, or even the fact that they function well, is something of a mystery in terms of orthodox electrochemical principles. In fact, one of the active and prominent workers in the ISE field, Prof. A. Rechnitz of SUNY Buffalo, referred to coated wire electrodes as "these improbable devices" in his plenary lecture

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INTRODUCTION

The present investigation of the nature and mechanism of electrical conductivity of polymeric films incorporating various organic solvent-compatible salts and complexes was inspired initially by our research in the area of ion selective electrodes. Ion selective electrodes (ISE), one of the most exciting recent developments in electrochemistry, permit rapid, reliable, selective, and sensitive potentiometric sensing of a wide number of inorganic (1, 2) and organic (2) cations and anions as well as of ionogenic species (e.g., of CS_2 ; $\text{CS}_2 + \text{R}_2\text{NH} \rightarrow \text{R}_2\text{NCS}_2^+\text{H}^+$) (3). In the course of our ISE work we discovered that a metallic conductor (Cu, Pt, Ag, etc.), when coated with a thin polymer film (PVC, polymethylmethacrylate, epoxy) in which a suitable organic-soluble salt was dissolved, would serve as an ion selective electrode in a manner equivalent, or in many cases, (4, 5) superior to the conventional "barrel" type of "liquid membrane" ion selective electrode. Our ion selective electrodes, termed "coated wire" electrodes, have the further structural advantages of simplicity and concomitant very low cost, of ruggedness so that they can be used in various field applications (including in situ oceanographic measurements as will be described later), and of miniaturization to a point where they could serve in intracellular measurements. Having no internal reference solution, the coated wire electrodes can be placed in any attitude (the barrel type must be mounted vertically or nearly so).

The mechanism of electrode behavior of the coated wire electrode, or even the fact that they function well, is something of a mystery in terms of orthodox electrochemical principles. In fact, one of the active and prominent workers in the ISE field, Prof. G. Rechnitz of SUNY Buffalo, referred to coated wire electrodes as "those improbable devices" in his plenary lecture

at the International Conference on ISE at Cardiff, Wales in 1972. Although no internal reference solution is present to establish a fixed potential at the interface between the metallic conductor and the under side of the polymer film, some other means of providing a relatively constant potential at that interface must exist for the electrode to function as well as it does.

Another puzzling aspect of the coated wire electrodes is the means of charge conduction across the film. An examination of the electrical conductivity of such films led to the discovery of their exceptionally high temperature coefficient and to their possible use as polymeric thermistors. Research under this contract was initiated to explore this phenomenon and its underlying reasons.

A further extension of the research involved examination of coated wire electrodes involving the so-called "neutral carriers". These are of interest from a number of points of view - (a) the ions involved, such as K^+ , have great relevance to problems of oceanographic analysis (6); (b) the systems are quite similar to those involved in transport of ions in biochemical membranes; (c) the concentrations of the very expensive reagents used in the polymeric films are so low that proper functioning critically requires the incorporation of suitable plasticizers in the film. In these systems we wanted to address ourselves to fundamental questions having important practical implications. For example, failures of potassium electrodes have been observed when the temperature of measurement is lowered. Does this coincide with the so-called glass transition temperature of the polymer? Examination was also planned of the dielectric constant of various film compositions as a function of temperature to explore this and alternate explanations. The effect of plasticizers on various polymeric film electrodes has been reported to be variable

and unpredictable. A systematic study would be undertaken to resolve such conflicting evidence and to develop a rational set of guidelines outlining the effects that can be expected and how to optimize their use in developing properly functioning electrodes. We planned to interface our polymer film conductivity experiment to a minicomputer in a manner that would not only improve the quality of the data required in the determination of "steady-state" conductivity and its temperature coefficient, but would also permit a more quantitative and useful examination of transient phenomena occurring in the first second or two. Study of such transients will present an opportunity to obtain further discriminating evidence in the nature of the charge conduction process(es) in the polymer films.

The following technical reports have been published describing the research arising from this grant:

Technical Report #1, 1 March 1973, "Conductance of Quaternary Ammonium Salt Dispersions in Polymeric Films". This was also published in Anal. Chem. 45, 1975 (1973). Abstract of this report:

Solutions of quaternary ammonium salts in polymeric materials exhibit unusually high temperature coefficients of electrical conductivity. Experiments

are described which indicate that conduction might be produced through a combination of electronic and ionic mechanisms. The materials studied show promise as "throw-away thermistors". The results

shed some light on the mode of behavior of the recently developed coated wire ion selective electrodes.

Technical Report #2, 4 October 1974, "Polymeric Thermistors". Abstract of this report:

Conductance studies at various temperatures and

pressures have been carried out on polymeric films of PVC and epoxy containing quaternary ammonium chlorides and selected plasticizers. In addition, dielectric constants measurements have been made on these materials. The work is discussed in terms of its bearing on the mechanism of electric conduction in filled polymeric films.

Technical Report #3, 6 April 1975, "Electrical Charge Conduction Mechanism in Polymer Membrane Ion Selective Electrodes". This was also published in Anal. Chem., 47, 2249 (1975). Abstract of this report:

A study of the temperature (20°-80°C) and pressure (1-2000 atm) dependence of quaternary ammonium salt-containing polymeric membranes used in ISEs was undertaken to elucidate the mechanism of charge conduction. Conductance activation volumes of 60-80 cm³ and a linear log σ_{25} vs. $1/c$ strongly indicates an ionic mechanism of charge conduction in these membranes. The high conductance activation energies observed cannot be exclusively linked to electronic modes of charge conduction.

Technical Report #4 - missing due to my mistake in numbering.

Technical Report #5, 10 December 1976, "Electrical Conductivity of Ion Exchange Resins". This was also published in Anal. Chem., 49, 767 (1977).

Abstract of this report:

The electrical conductivity of Dowex-1 in the Cl⁻, Br⁻, I⁻ and NO₃⁻ forms have been determined at pressures ranging up to 2000 atmospheres. Activation volumes for the conduction process closely match the crystallographic volumes of the anions. The data sheds light on the conduction mechanism in ion selective electrodes employing polymeric membranes.

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In addition, the following work not previously described in technical reports or publications arising from this grant will be described:

I. Electrical Behavior of Potassium Valinomycin/Polymer Films.

A. Effect of Plasticizer

1. Background

Electrical properties of polymeric mixtures incorporating the macrotetrolide antibiotic valinomycin are of current great interest because of their widespread use in potassium ion selective electrodes. In a number of studies reported in the literature, the performance of these electrodes was found to be critically dependent on electrode membrane composition. The ratio of plasticizer to polymer has to be carefully selected and strictly controlled. Further, the plasticizer used demonstrated a dual role: it acted both as a "mediator" or solvent for the valinomycin as well as a polymer softening agent, presumably permitting greater diffusion in the polymer.

The mechanism by which temperature affects the performance of these membranes is not known, yet many electrodes fail to function at temperatures of less than 10°C. Speculation has been offered that electrical conductivity may proceed through a protonic mechanism (7), yet little evidence exists to support these assumptions.

In this study of the potassium-valinomycin (K^+-Val) polymer systems, the effect of plasticizer on electrical conductivity over a wide temperature range was studied.

2. Experimental

Preparation of K⁺-Val

100 mg of valinomycin (Sigma Chemical Co.) was dissolved in 10 ml of chloroform and shaken twice for four hours with an aqueous solution containing 0.1M KCl. To assure quantitative loading with K⁺ ion, a third shaking using 1M KCl for eight hours was performed. The organic phase was thoroughly washed with water and then evaporated to dryness.

Preparation of K⁺-VAI/Polymer Samples

Samples were prepared with the following compositions:

Polymer	% Plasticizer
Polyvinylchloride	30-70% di(ethylhexyl) adipate (DOA)
"	30-70% dioctylphthalate (DOP)
Polystyrene	50-70% DOA
"	50-70% DOP
Polymethylmethacrylate	50% DOA

All samples contained 1 mg valinomycin/ml of 5% polymer solution.

Triplicate samples were prepared for each composition. In addition, samples containing no plasticizer were prepared.

Electrical Conductivity Measurements

Electrical current was measured using applied voltages between 10-300V (usually, 100V) over a temperature range of -22°-80° (except when necessary, 0-75° was used).

The computer controlled system was used in data acquisition and subsequent processing.

3. Results and Discussion

Computer plots of the data as $1/T$ vs $\log R$ show at least two distinct linear regions with the data from some samples having a third linear region.

For the lower temperature regions, a slope of ca. 0 exists while for the higher temperature region the slope is greatly increased. Such behavior has been reported in the literature (8) and the inflection point has been shown to be the glass transition temperature, T_g .

The results for the DOA plasticized system are summarized in

Table I.

Table I. Effect of Di (2-ethylhexyl) Adipate (DOA) on Electrical Conduction of K⁺-Val/PVC¹

Wt% DOA	Volume % DOA	$T_g(^{\circ}\text{C})$	$E_a(\text{eV})$	
			$<T_g^2$	$>T_g^3$
0	0	45	0	2.3
30	23	26	"	1.5
50	42	3	"	1.3
70	63	-14	"	3.4

¹ 1.0 mg/5.0 mg PVC

² E_a for all samples was ca .0 within expt. error

³ region of largest slope

The lowering of T_g by increasingly higher concentrations of DOA is consistent with normal polymer behavior (9). A plot of volume % of DOA vs. T_g is (Fig. 1) also linear as is often observed for plasticized polymers.

The extremely large difference in activation energy, E_a , for the regions below and above T_g is unusual. The value for the region above T_g is quite similar to results reported for the quaternary ammonium salts. An important exception is the extremely unusual behavior of the 70% DOA sample, whose E_a of 3.4 eV is among the highest measured, yet it has a conductivity at

25° estimated to be 10^{-6} (ohm cm). The near zero value of activation energy at temperatures below the T_g definitely suggests a completely different mode of conductivity. The E_a value is consistent with those generally observed for electronic inorganic semiconductor systems (like CdS).

Studies comparing other plasticizers with DOA reveal that it is the most effective in reducing T_g (Table I).

Table II
Comparison of T_g for PVC/K⁺-Val
Containing 70 wt% Plasticizer

Plasticizer	T_g
Diethyladipate	-25°
Dibutylsebacate	15°
Dibutyladipate	17°
Diphenylphthalate	28°
Diethylphthalate	33°

B. Pressure-Conductivity Studies

Our previous work (10) on the study of the pressure dependence of the conductivity of the impregnated polymer films was extended to the plasticized valinomycin films. Initially, considerable difficulty was experienced due to the relatively high sample resistance, e.g., $>10^{10} \Omega$. Super-thin

(0.001 cm) films were recast but electrical shorting of the electrodes was a common problem; however, sample resistances were lowered to 10^8 - $10^{10} \Omega$. The pressure dependence of the resistance was measured in the apparatus previously described.

The following variations in film composition were used: 1.0 mg of potassium valinomycin or valinomycin itself (referred to as loaded or unloaded,

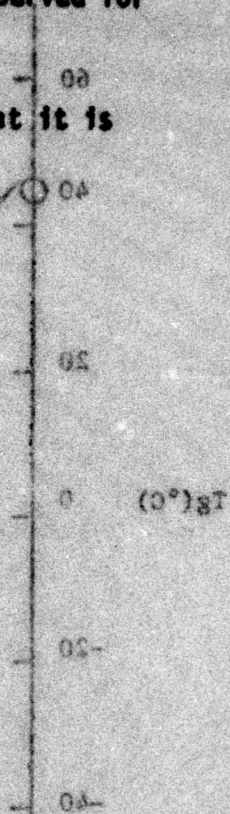
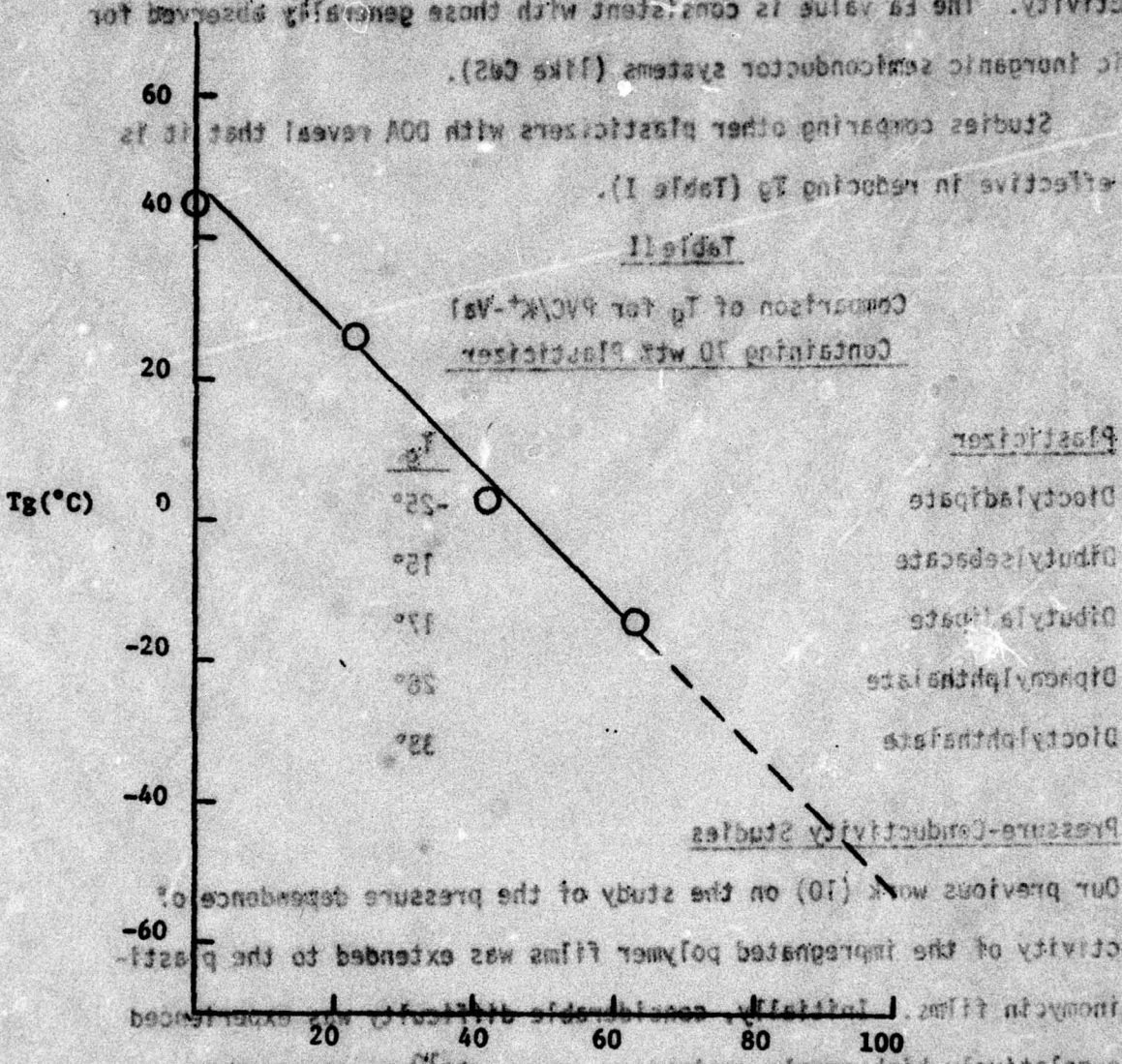


Figure 1. Effect of Plasticizer on the Glass Transition Temperature T_g of Polyvinylchloride-valinomycin.



The following variations in film composition were used: 1.0 mg of potassium valinomycin or valinomycin itself (referred to as loaded or unloaded, a common problem; however, sample resistances were lowered to $10^8-10^{10} \Omega$). The pressure dependence of the resistance was measured in the apparatus previously described.

Our previous work (10) on the study of the pressure dependence of the conductivity of the impregnated polymer films was extended to the plasticized valinomycin films. Initially, considerable difficulty was experienced due to the relatively high sample resistance, e.g., $>10^{10} \Omega$. Super-film (0.001 cm) films were recast but electrical shorting of the electrodes was

respectively), 50 mg PVC with 20-40% dioctyladipate (DOA). These films were cast from tetrahydrofuran.

Table III. Results

PVC Sample	% DOA	T_g Expected	ΔV^\ddagger	Log $R_{25^\circ, 1atm}$
Loaded	40	0	39	8.2
Unloaded	40	-0	42	8.1
Loaded	30	8°	+54	9.3
Unloaded	30		47	8.8
Loaded	20	33°	--	9.8
No VAL	40		44	10.0
No VAL	20		--	>10.3
"Pure" PVC			--	15.0 $\Omega \cdot cm$
PVC alone*			--	15.8 $\Omega \cdot cm$

*Saito, et. al., J. Polymer Sci., 6, 1297 (1968)

Precision ΔV^\ddagger = ±5%, Log R = ±0.2

Effect of Plasticizer

A number of features can be summarized from the table:

- (1) both loaded and unloaded valinomycin show similar behavior;
- (2) ΔV^\ddagger seems to be dependent only on PVC/DOA composition;
- (3) samples containing valinomycin gave greater conductivity est., 0.7-1.8 log units.

Although the determined ΔV^\ddagger 's appear not to be a function of valinomycin content, those samples which had valinomycin in them gave bulk conductivities which were much greater than plasticized PVC. One can therefore conclude that valinomycin participates in the conduction mechanism despite the fact that the experimentally determined ΔV^\ddagger is consistent with processes involving segmental motion in PVC. Further the measured ΔV^\ddagger agrees closely with that reported for "pure" PVC.

42 cm³/mole. Two possible overall conduction mechanisms can be postulated with regard to the $\Delta V^{\#}$ found.

1. The valinomycin provides charge carriers which coincidentally have a $\Delta V^{\#}$ of ca. 40-50. Sources of charge carriers which would give such a $\Delta V^{\#}$ are numerous: low MW impurities, conformational changes in the VAL structure, associated inorganic ions.

2. A somewhat more likely mechanism is that valinomycin provides a source of charge carriers which are dependent upon segmental polymer motion for their mobility. Specifically, this could involve the production of hydrogen atom (protons?) current-carriers from valinomycin which move along the polymer chain by a hopping or dissociation mechanism. Such a segmental motion-facilitated transport of protons has been suggested as the current-carrying mechanism in polyamides.

II. Electrochemical Behavior of Potassium Valinomycin/Polymer Films

Effect of Plasticizer

The earliest valinomycin based-K⁺ ion selective electrodes (ISE's) were of the liquid membrane type and employed diphenylether as a solvent (11, 12, 13). A disadvantage of this system is that diphenylether has a melting point at 28°C and it has been noted that "frozen" membranes do not respond to potassium (13, 14). Similarly, it was noted by Fiedler and Ruzicka (14) that for a polymer membrane electrode to function the glass transition temperature (T_g) of the membrane must be well below room temperature.

The T_g of a polymer membrane may be altered by incorporating a plasticizer in the membrane. For PVC-valinomycin membranes dioctyladipate (DOP) is a good plasticizer. By incorporating a sufficient amount of DOP in a PVC-valinomycin membrane (generally 40 w/v% is used) electrodes that function at

room temperature and well below can be made. Addition of too much plasticizer, however, yields membranes that will not dry completely at room temperature which is, of course, undesirable.

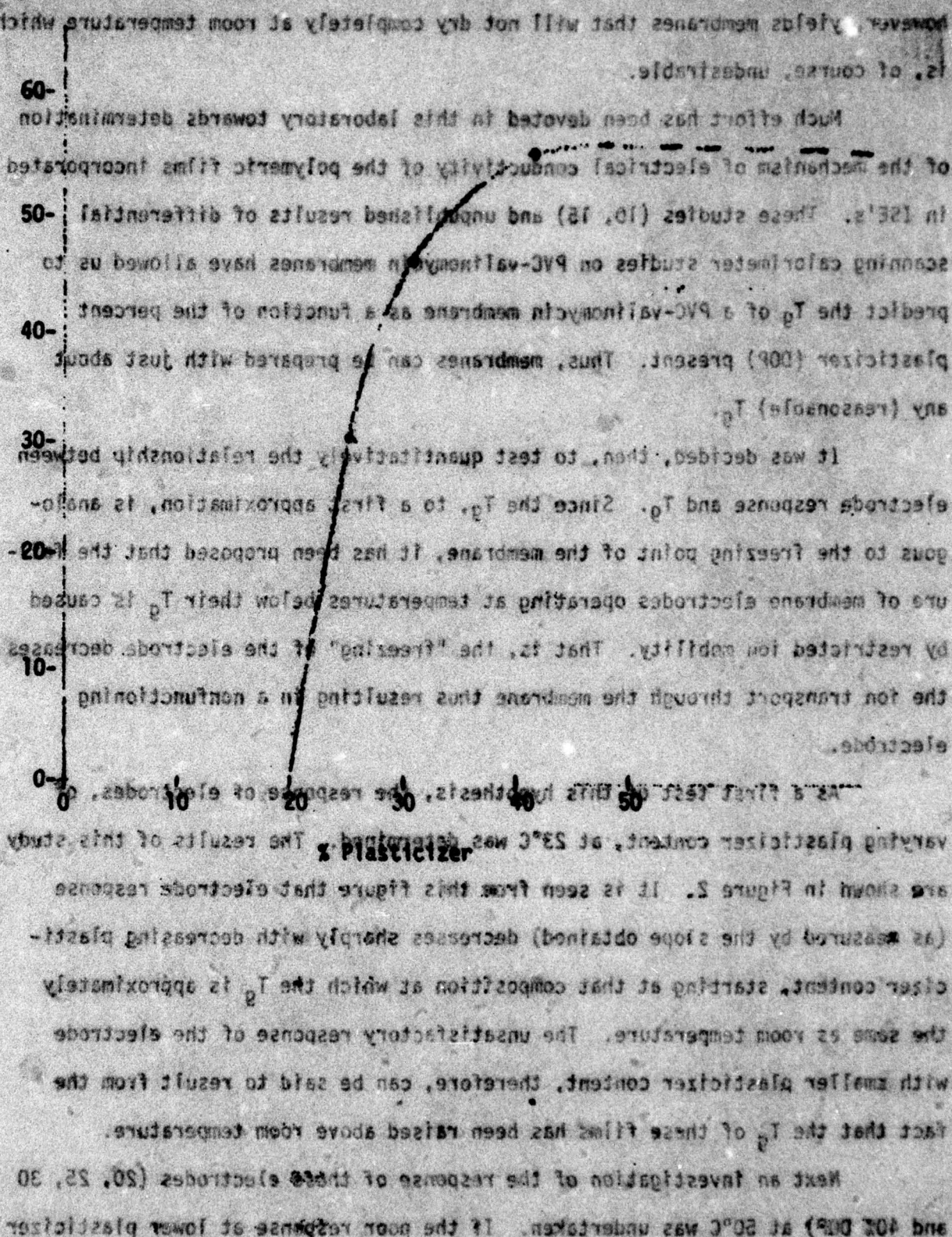
Much effort has been devoted in this laboratory towards determination of the mechanism of electrical conductivity of the polymeric films incorporated in ISE's. These studies (10, 15) and unpublished results of differential scanning calorimeter studies on PVC-valinomycin membranes have allowed us to predict the T_g of a PVC-valinomycin membrane as a function of the percent plasticizer (DOP) present. Thus, membranes can be prepared with just about any (reasonable) T_g .

It was decided, then, to test quantitatively the relationship between electrode response and T_g . Since the T_g , to a first approximation, is analogous to the freezing point of the membrane, it has been proposed that the failure of membrane electrodes operating at temperatures below their T_g is caused by restricted ion mobility. That is, the "freezing" of the electrode decreases the ion transport through the membrane thus resulting in a nonfunctioning electrode.

As a first test of this hypothesis, the response of electrodes, of varying plasticizer content, at 23°C was determined. The results of this study are shown in Figure 2. It is seen from this figure that electrode response (as measured by the slope obtained) decreases sharply with decreasing plasticizer content, starting at that composition at which the T_g is approximately the same as room temperature. The unsatisfactory response of the electrode with smaller plasticizer content, therefore, can be said to result from the fact that the T_g of these films has been raised above room temperature.

Next an investigation of the response of these electrodes (20, 25, 30 and 40% DOP) at 50°C was undertaken. If the poor response at lower plasticizer

Figure 2. Average Slope vs. Percent Plasticizer at Room Temperature.



contents is. Indeed, due to the higher T_g of the polymer film, then making measurements at a temperature above the T_g should result in improved behavior.

III. Thermistor Applications.

At present, nearly all commercially available thermistors are fabricated from semiconducting metal oxides (16). These materials are expensive as well as being susceptible to damage (the majority are sealed in fragile glass beads).

The previously measured, rather large, negative temperature coefficient possessed by quaternary ammonium compounds dispersed in polymeric mixtures suggests that they may be useful as sensitive temperature probes. Such materials would have great advantages in terms of ease and reliability of fabrication, and possibility of a relatively wide and continuous range of variation of properties. In addition, these thermal sensitive resistors could be fashioned in a great variety of geometries in order to meet the unique specifications that might be demanded in biological and environmental sensing situations.

A number of relationships exist in the thermistor field for describing the behavior and sensitivity of these devices:

$$R_{25} = R_1 \exp \left[\beta \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

where β is a term similar to E_a in the equation $\sigma = \sigma_0 \exp(-E_a/2kT)$. A temperature coefficient of resistance α , is defined as:

$$\alpha_{25} = \frac{1}{R_{25}} \cdot \frac{dR}{dT}$$

where α_{25} is the percent change in resistance for a 1° change in temperature, centered at 25°. Commercial thermistor devices have α values which range from -3 to -5% with corresponding resistances of typically 10^6 ohms or less.

Table IV lists the α values expected for the activation energy range

0.5-4.0 eV, covering the extremes found for the materials used in this study. As is evident in this table, α_{25} values are generally much greater for the substances studied than those commonly present for commercial devices. The change in resistance for the 3-4 eV materials is particularly dramatic for 10° changes in temperature (362-1310%).

Table IV. Percent Change in Resistance for Various E_a Values.

E_a (eV)	ΔT ($^\circ C$)			
0.5	0.01	0.1	1.0	10.0
1.0	0.03	0.32	3.3	37
2.0	0.06	0.65	6.6	68
3.0	0.13	1.30	13.7	254
4.0	0.19	1.90	21.3	568
	0.26	2.60	29.4	1190

As would be expected for any ionic conducting device, long-term drifts of resistance (time-dependent polarization) would cause problems for detecting small resistance changes. However, in an automated polymeric thermistor device, long-term drift can be compensated by a "feed-back" operational amplifier loop with a relatively long time constant (say 20 min). In some cases, the long-term drift of resistance was reduced to ca. -1 %/h by the selection of an appropriate polymeric mixture (low concentrations of electro-active materials in epoxy), although the resistances encountered for these mixtures was so large (10^{12} ohm) as to make measurements difficult. Short-term instability, however, posed much more serious limitations (Table V) on the use of these materials as temperature probes.

Table V. Comparison of Polymeric Thermistors to Commercial Devices.

Polymeric thermistor	15	±0.5	60
Allied thermistor network	4	±0.005	2

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Personnel (other than Principal Investigator)

1. Gary B. Carmack - Graduate Research Assistant 9/72 - 6/77
Ph.D., University of Arizona, 1977
(Present Position: Postdoctoral Research Associate with Prof. Merle Evenson
Medical School
University of Wisconsin
Madison, Wisconsin)
2. Charles R. Martin - Graduate Research Assistant 8-75 - present
Ph.D., expected University of Arizona, Fall 1979
3. Robert W. Cattrall - Postdoctoral Research Associate 7/77 - 1/78

Present Position: Associate Professor
Department of Chemistry
La Trobe University
Bundoora, Victoria, Australia

PUBLICATIONS ARISING OUT OF THIS RESEARCH

1. G. D. Carmack and H. Freiser, "Conductance of Quaternary Ammonium Salt Dispersions in Polymeric Films", *Anal. Chem.*, **45**, 1975 (1973).
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